Fluorescence Detection from Single Dendrimers with Multiple Chromophores

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J(H,H) = 9.8 Hz, 4H; H_{arene}), 6.60 (d, ^4J(H,H) = 1.0 Hz, 2H; *ortho*-$H_{quinone}$), 6.37 (d, ^3J(H,H) = 4.4 Hz, 2H; *meta*-$H_{quinone}$), 6.14 (d, ^3J(H,H) = 9.8 Hz, 4H; H_{arene}), 1.91(m, 4H; OCH_2), 1.75 (m, 4H; OCH_2CH_2), 1.62 (m, 4H; $OCH_2CH_2CH_2$), 1.58–1.32 (m, 68H; H_{alkyl}), 1.04–0.94 (m, 12H; CH_3); ^{13}C NMR (125 MHz, [D$_8$]THF): δ = 185.98 ($C_{quinone}$), 161.75 (C_{arene}–O), 161.36 (C_{arene}–O), 147.32, 145.05, 140.90, 137.00, 135.94 130.60 (all C_{arene}), 58.57 (OCH_2), 34.08, 31.82, 31.45, 28.25, 24.75 (all C_{alkyl}), 15.63 (CH_3); MS (FD, 8 kV): m/z (%): 1300.4 (100) [M^+] (calcd for $C_{90}H_{122}O_6$ = 1300.0); IR (KBr pellet): $\tilde{\nu}$ [cm^{-1}] = 3062(w), 3041(w), 2918(s), 2847(s), 1663 [$(CO)_{stretch}$], 1603(m), 1495(m) [ν(C=C)$_{arene}$], 1244(s) [(Ar–O–R)], 1170(m), 825(m); UV/Vis ($CHCl_3$): λ[nm] (lgε [L mol^{-1}cm^{-1}]): 314 (sh, 4.52), 330 (4.69), 347 (4.74).

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Fluorescence Detection from Single Dendrimers with Multiple Chromophores**

Thomas Gensch, Johan Hofkens, Andreas Heirmann, Kenji Tsuda, Wendy Verheijen, Tom Vosch, Thomas Christ, Thomas Basché, Klaus Müllen,* and Frans C. De Schryver*

Following the pioneering studies of Moerner and Kador as well as Orrit and Bernard[1] a wealth of experiments have been performed using high-resolution single-molecule spectroscopy (SMS) at low temperature.[2] Single molecules that are immobilized on and in thin polymer films and gels, as well as on glass, have been investigated at room temperature with various types of optical microscopies.[3, 4] The spectroscopic study of single molecules in solution has attracted substantial attention and is currently being developed as a new tool in analytical chemistry.[5]

In the majority of the SMS studies the single molecules are investigated through their fluorescence properties. One of the most prominent observations in SMS studies is the occurrence of sudden changes in fluorescence intensity, often called the on–off behavior of a single molecule. This is in contrast to bulk measurements where the fluorescence intensity decreases exponentially with irradiation time as a result of photobleaching. Herein we investigate the difference between SMS of a single chromophore and of multichromophoric systems with the emphasis on the passage from the typical on–off behavior of a single molecule to the behavior of the ensemble. To this end a system has to be synthesized in which chromophores can be placed at a specific distance without being coupled through bonds. One way to obtain multiple chromophores in a well arranged environment is based on dendrimer synthesis.

We have recently introduced a new type of dendrimers and hyperbranched 3-dimensional polyphenylenes consisting of penta- or hexaphenylbenzene building blocks with strongly twisted benzene units.[6, 7] The polyphenylene dendrimers are synthesized by repetitive Diels–Alder reactions using ethynyl-substituted aromatic cores such as 3,3′,5,5′-tetraethynylbiphenyl (**1**) and the cyclopentadienone derivative **2** as the branching (A_2B-type) reagent. The stepwise approach to

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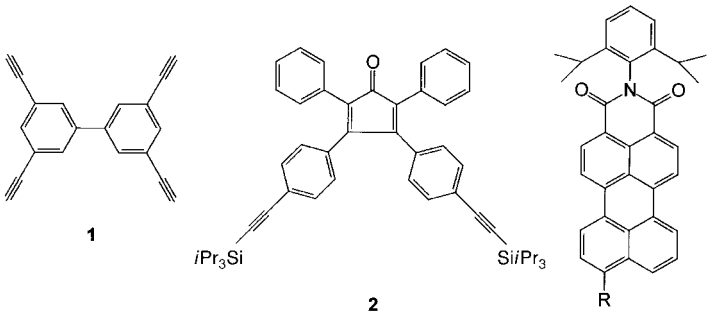
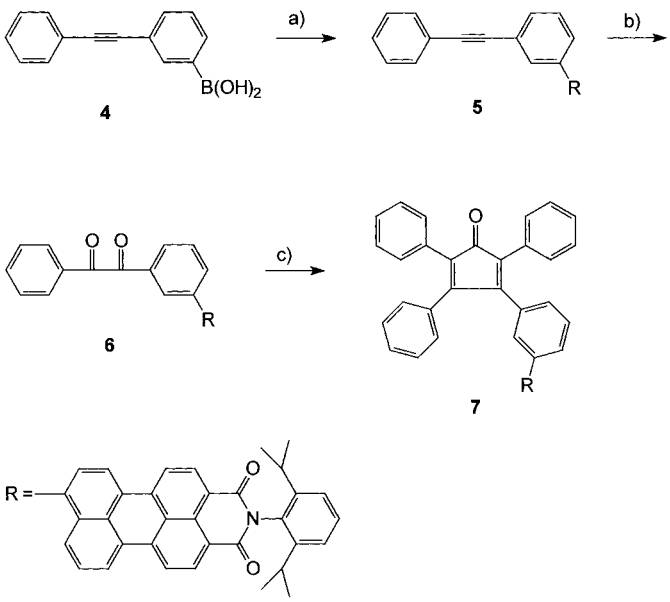
building successive generations of dendrimer rests upon the following: in the reaction of **1** with **2** the latter acts only as diene if its ethynyl functions are sterically blocked by triisopropylsilyl groups, but the dienophile functions can be "activated" by removal of the silyl groups with tetrabutylammonium fluoride. The final Diels–Alder reaction can be used to attach functional groups to the surface of the dendrimer. Although the polyphenylene framework does not serve as a chromophore in its own right at our excitation wavelength, a defined number of chromophore molecules can be attached to the outer rim of the dendrimer to form unique nanoemitters. We have chosen the perylenedicarboximide **3a** as the

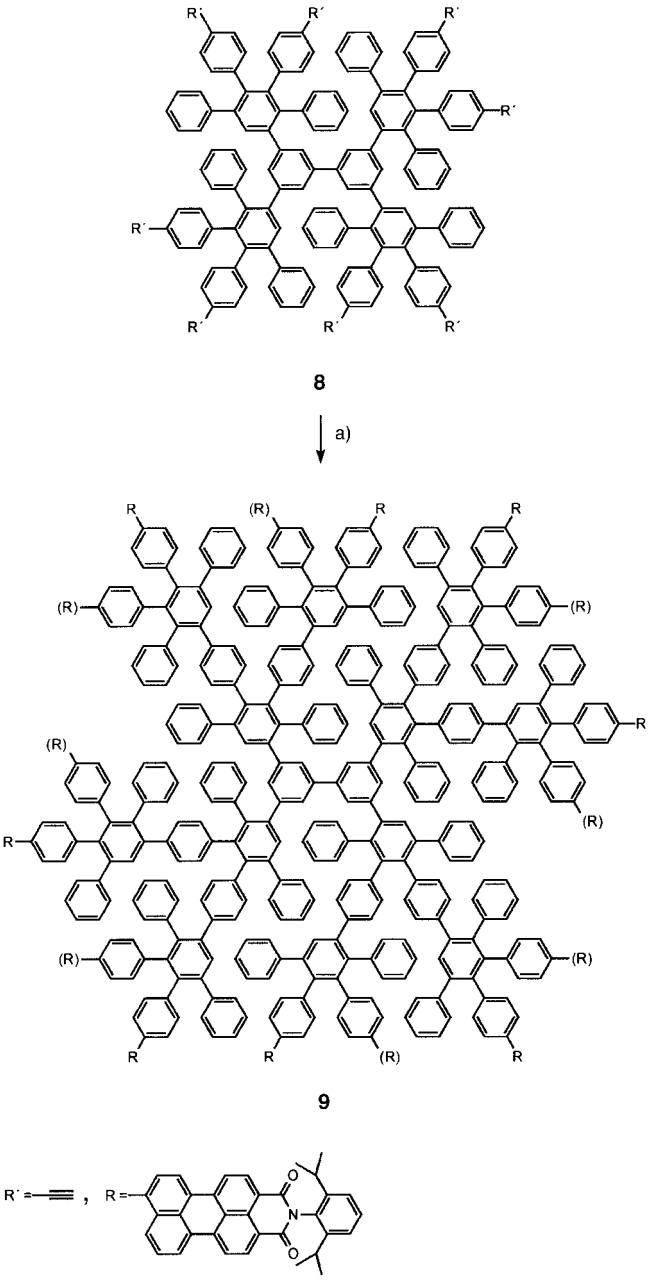


chromophore because of its photostability, its absorption wavelength (around 500 nm), its high absorption coefficient, and its high fluorescence quantum yield ($\Phi_F = 0.90$). Its bromoderivative **3b** is coupled to **4** in a Suzuki[8] reaction and the resulting diarylacetylene **5** transformed into the corresponding α-diketone **6**, which then affords the functionalized cyclopentadienone **7** (Scheme 1).

The Diels–Alder cycloaddition of **7** with the core molecule **1** leads to the first generation of a polyphenylene dendrimer carrying four fluorophores, for which single molecule spectroscopy measurements will be reported elsewhere. The analogous Diels–Alder reaction of **7** with dendrimer **8** produces the higher homologue **9**, that is, the second generation dendrimer with eight fluorophores covalently bound to the dendrimer rim (Scheme 2). The two possible



Scheme 1. a) **3b**, 5 mol% [$Pd(PPh_3)_4$)], toluene, 2 M K_2CO_3, ethanol, 120 °C, 12 h, 72%; b) I_2, DMSO, 150 °C, 12 h, 85%; c) diphenylacetone, *n*-tetrabutylammonium hydroxide 0.8 M, toluene, 90 °C, 1 h, 68%.



Scheme 2. a) 12 equiv **7**, diphenyl ether, tetraethyleneglycol, 195 °C, 82%. (R) = alternative positions of substituents R.

regiochemically different courses of the Diels–Alder reaction of **7** means there is some structural ambiguity in **9**. This, however, does not hamper the photophysical characterization given below since the photophysical study in solution leads to averaged information and does not affect the analysis at the single-molecule level. The structural proof of **9** came from the MALDI-TOF mass spectrometric analysis which supports the existence of the defect-free transition from the first to the second generation dendrimer.[9] As a model compound for **9**

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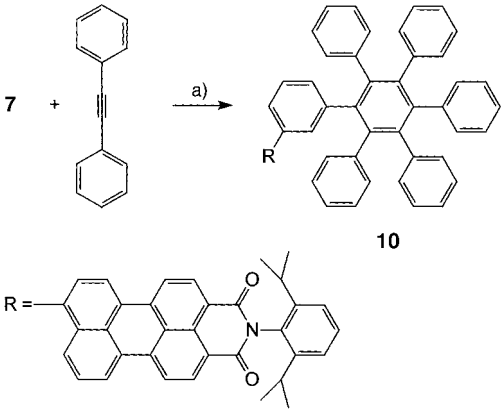
we have also synthesized the hexaphenylbenzene **10** in which only one peryleneimide chromophore is attached (Scheme 3).[9]



Scheme 3. a) Diphenyl ether, 260 °C, 85 %.

The determination of the absorption and fluorescence spectra of **10** and **9** by SMS allows the comparison of the fluorescence behavior of a single chromophore and eight chromophores in a single molecule. (Figure 1). The absorption spectrum of compound **9** is slightly broadened at the red edge of the spectrum (width at half peak height = 3100 cm^{-1} for **10** and 3300 cm^{-1} for **9**) and has less fine structure around 515 nm compared to that of **10**. The fluorescence properties of

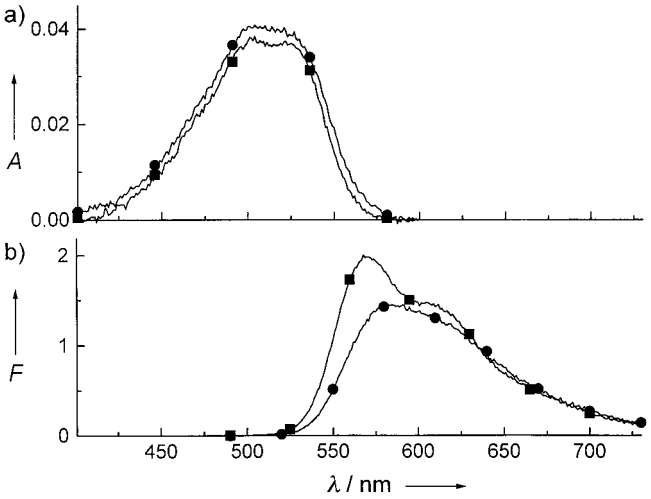


Figure 1. Absorption (a) and fluorescence spectra (b, excitation at 508 nm) of **10** (■) and **9** (●) in chloroform.

9 are also distinctively different: the spectrum shows less structure (see Figure 1), the quantum yield is lower, and the fluorescence decay is multiexponential, with a decay time equal to that of **10** as a major component and at least two additional components (Table 1). The differences between the absorption spectrum of **9** and **10** in solution indicate an interaction of some of the eight peryleneimide chromophores already occurring in the ground state. In a recent study devoted to the dynamic behavior of **9** and **10** in solution several processes were identified for **9** which were absent for **10**. These processes, with characteristic times ranging from several picoseconds up to nanoseconds, were attributed to excitation transfer processes between two or more of the eight chromophores and interactions between excited states.[10]

Table 1. Fluorescence properties of **10** and **9** in bulk solutions and as single molecules.

Compound	Φ_F	τ_F [ns][a]	N_{sm}	$t_{survival}$ [s][b]	n [s^{-1}][b,d]	ε [$mol^{-1}\,cm^{-1}$][c]
10	0.80	4.2 (100 %)	81	70	1200	35000
9	0.65	0.25 (25 %) 4.2 (60 %) 7.5 (15 %)	74	250	3500	240000

[a] Measured at 570 nm, $\chi^2 < 1.1$; the normalized relative amplitudes are given in parentheses. [b] Average value for all single molecules N_{sm}. [c] Measured at 495 nm. [d] Maximum dwelling rate.

The confocal fluorescence microscopy images of polymer films produced from dilute solutions of **10** and **9** in polyvinylbutyral (PVB) typically show 10 to 25 spots corresponding to single molecules of **10** and **9** on a $5 \times 5\ \mu m^2$ area. The images of **9** are three-to-fourfold as intense and exhibit a clear on–off behavior ("blinking") relative to **10**, which displays almost uniform spots exclusively (Figure 2 and Table 1). The

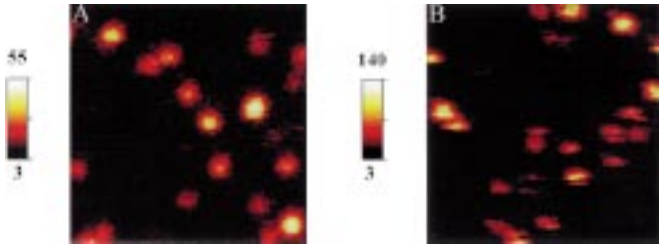


Figure 2. Confocal fluorescence images ($5 \times 5\ \mu m^2$, scale in counts per 10 ms; $\lambda_{exc} = 543.5$ nm, linear polarized light, $P = 200\ W\,cm^{-2}$, 10 ms dwell time per pixel) of single molecules of compound **10** (A) and compound **9** (B) in a PVB film.

fluorescence transients, that is, the fluorescence intensity of a single molecule as a function of time, are obtained by positioning the excitation beam on a fluorescent spot in the images of single molecules of either **10** or **9**. The number of single molecules thus studied is 81 for **10** and 74 for **9**. Typical transients are investigated by visual inspection as well as by a histogram analysis (Figure 3). On–off behavior as well as jumps between different emissive levels are detected for both molecules. The observations are, however, very different for **10** and **9**. Transients of single molecules of **9** show more levels, more jumps, and longer survival times compared to those of **10** (see Table 1 and Figure 3). If the eight chromophores of **9** absorbed and emitted independently from each other one would expect mainly jumps between neighboring intensity levels. For many of the fluorescence transients of **9**, however, jumps from levels of high to low fluorescence intensity (including the zero level) and vice versa are observed. These jumps suggest the existence of strong electronic interactions between several peryleneimide chromophores within one dendrimer and supports the interpretation of the bulk solution studies.[10]

The different fluorescence levels could result from different processes: rotational and spectral diffusion, electronic coupling or decoupling of the single chromophores (only for **9**), a changed population of the short-living off-states (relative to the dwelling time of 10 to 50 ms) such as triplets or

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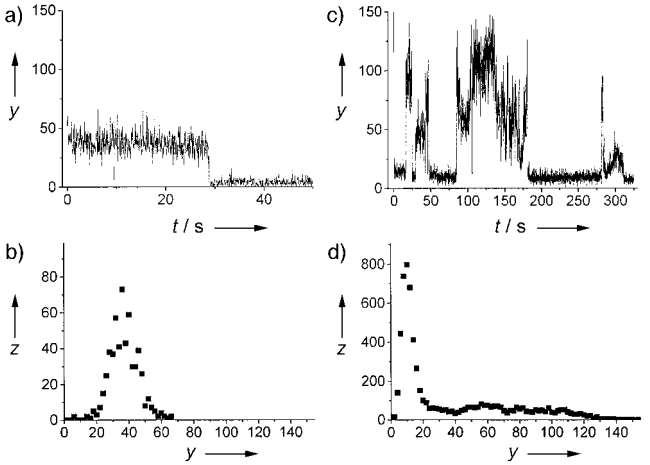

Figure 3. Fluorescence intensity transient (y, 50 ms dwell time) of compound a) **10** and c) **9** as well as the corresponding histograms (z = frequency of occurrence of a certain count rate) of the transient of b) **10** and d) **9**.

reversible photochemical reactions. Spectral jumps are a likely source of dynamics in the fluorescence transient since the excitation is performed in the red edge of the absorption spectrum of **10** and **9**. Therefore for a detailed investigation series of spectra of single molecules (30 for each compound) were recorded (Figure 4). A comparison of the spectra showed that there was a shorter survival time of **10**, but most of the spectra of **10** showed a uniform spectral shape with a vibrational fine structure similar to the solution spectra and only small differences in the emission maximum. However, the spectra of **9** are distinctively different for individual molecules, with the spectral shape ranging from broad, unstructured bands similar to the solution spectrum of **9** to spectra with vibrational fine structure similar to **10** in solution. Additionally, large differences in the wavelength of maximum fluorescence (from 560 nm to 595) were observed.

It is rather exceptional to observe these various spectral types and spectral shifts within the life time of individual molecules. The spectra reported in Figure 4 b for a molecule of **9** starts with a broad, unstructured red-shifted spectrum, which is followed by a large blue shift within 40 s and accompanied with the development of a spectrum with fine structure. After another 30 s it adopts a broad spectral band shape with a blue-shifted maximum relative to the first spectrum. Within the next 90 s some minor spectral changes occur with only small changes in intensity, and at 160 s an irreversible photoreaction leads to a nonemitting photoproduct of **9**. This nonemission could be the result of the photoproduct having a low fluorescence quantum yield as well as a large shift of the absorbance spectrum, which prevents excitation at 543 nm. The fact that single dendrimers of **9** show fluorescence spectra similar to those of **10** can be explained by a loss of the electronic interactions between the perylene-imide chromophores within one dendrimer. This situation can be either static, in which molecules of **9** show only the structured spectrum, or dynamic, in which molecules of **9** switch back and forth between the two spectral shapes. Finally, the measurement of the series of fluorescence spectra explains at least partially the larger dynamics in the fluorescence intensity transients of **9** relative to **10**.

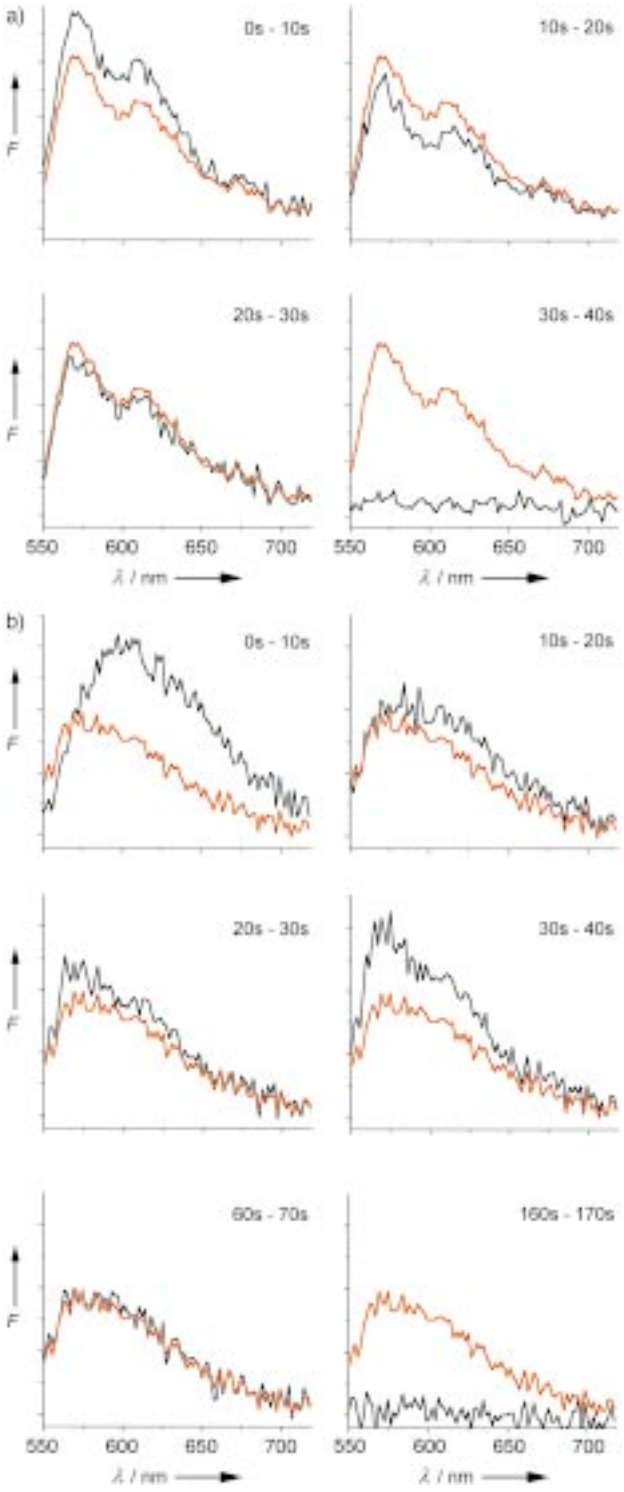

Figure 4. Sequence of fluorescence spectra (10 s integration times) for a single molecule of a) **9** and b) **10**. The red line represents the average fluorescence spectrum integrated over the analysis time of the investigated single molecule.

Compounds **10** and **9** together with other generations of this and similar dendritic structures with multiple chromophores are currently under investigation, both in bulk solutions and on the single-molecule level, using different fluorescence and absorption spectroscopic techniques. These studies offer the possibility of closing the gap between single-molecule studies on single chromophores[11] and multichromophoric systems

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such as fluorescent polymers, phycoerythrocin, and light-harvesting protein complexes from the photosynthetic apparatus.[12] The synthetic approach chosen here offers ease of variation and control of the number of chromophores as well as their interactions and therefore the possibility of tailoring molecules for single-molecule spectroscopy.

Experimental Section

Preparation of the PVB films: Solutions of **10** or **9** (10^{-9} M) in chloroform were mixed with a solution of polyvinylbutyral (3 mg mL^{-1}) in chloroform. These mixtures were spin-coated on a cover glass at 4000 rps to yield 10 nm thick polymer films. The sample preparation included a careful cleaning of all glassware used for the sample and polymer solutions and the cover glasses by sonication in acetone, sodium hydroxide (10%), and milliQ water.

The absorption spectra were measured on a Perkin-Elmer Lambda-6 and fluorescence spectra on a SPEX Fluorolog 1680. The time-resolved fluorescence SPT apparatus with 10 ps time resolution has been described elsewhere.[13]

The fluorescence of single molecules was detected using a confocal microscope (Diaphot 200, Nikon) with an immersion oil, high-numerical aperture (NA = 1.4) lens using an avalanche photodiode in the single photon counting mode (SPCM AQ151, EG&G) with suitable filters (Notch Plus 543.5, Kaiser Optics) as the detector. The fluorescence intensity transients were measured with dwell times of 10 to 50 ms. The fluorescence spectra were measured with a liquid-nitrogen cooled, back-illuminated CCD camera (LN/CCD-512SB, Princeton Instruments) coupled to a 150 mm polychromator (SpectraPro 150, Acton Research Cooperation) using 5 or 10 s integration times. The excitation source was a green continuous wave HeNe laser (543.5 nm, Melles Griot). Its randomized output was linearly polarized by using a Glan–Thomson polarizer. The excitation power density at the sample was between 100 and 500 W cm^{-2}.

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[9] **10**: ^{1}H NMR (300 MHz, $C_2D_2Cl_4$): $\delta = 8.56$ (d, $^3J = 9$ Hz, 2H), 8.38 (m, 4H), 7.40 (dd, $^3J = 7.8$ Hz, 2H), 7.25 (d, $^3J = 7.8$ Hz, 2H), 7.10 (dd, $^3J = 7.8$, 2H), 6.97–6.76 (m, 32H), 2.65 (m, 2H; CH(CH$_3$)$_2$), 1.08 (d, 12H; CH(CH_3)$_s$); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, spin-echo experiment): $\delta = 163.7$ (q; C=O), 145.4 (q), 143.7 (q), 140.9 (q), 140.4 (q), 140.3 (q), 140.2 (q), 139.8 (q), 139.5 (q), 137.7 (q), 137.6 (q), 132.7 (CH), 132.2 (q), 131.8 (CH), 131.4 (CH), 131.2 (CH), 131.0 (CH), 130.9 (q), 130.3 (q), 129.6 (CH), 128.9 (CH), 128.7 (q), 128.0 (CH), 127.8 (q), 127.7 (q), 126.9 (CH), 126.8 (CH), 126.6 (CH), 126.3 (CH), 125.0 (CH), 124.8 (CH), 123.7 (CH), 123.4 (CH), 120.5 (q), 120.4 (q), 120.1 (CH) 119.8 (CH), 28.8 (CH(CH$_3$)$_2$), 23.9 (CH(CH_3)$_2$); FD-MS (8 kV): m/z: 1011.7; calculated for $C_{76}H_{55}NO_2$: m/z: 1013.4. **9**: ^{1}H NMR (500 MHz), $C_2D_2Cl_4$): $\delta = 8.58–8.41$ (br, 32H), 8.37–8.15 (br, 64H), 2.78–2.76 (m, 32H), 1.18 (d, 96H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, spin-echo experiment): $\delta = 163.6$ (q, C=O), 145.3 (q), 143.2 (q), 141.1 (q), 140.2 (q), 139.6 (q), 138.8 (q), 138.0 (q), 137.7 (q), 137.4 (q), 137.2 (q), 137.0 (q), 132.0 (q), 131.4 (CH), 131.0 (q), 130.1 (q), 129.7 (CH), 129.0 (CH), 127.3 (CH), 126.7 (CH), 123.8 (CH), 120.2 (q), 28.9 (CH(CH$_3$)$_2$), 23.9 (CH(CH_3)$_2$); MALDI-TOF-MS: m/z: 8560.2; calculated for $C_{644}H_{450}N_8O_{16}$: m/z: 8556.4. Compounds **9** and **10** are seen by thin layer chromatography using different eluents as single fluorescence spots.

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